

Performance of internal reforming methanol fuel cell under various methanol/water concentrations

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Abstract Copper-based reforming catalyst was placed adjacent to ADVENT Technologies high-Temperature polymer electrolyte membrane/electrode assembly in a novel internal reforming methanol fuel cell (IRMFC) and tested for their electrochemical properties and chemical stability under various methanol/water anode feedstreams. Polarization measurements and AC impedance spectroscopy combined with measurements of reactor outlet composition were carried out. Methanol is being reformed inside the anode compartment of the fuel cell at 200 °C producing H₂, which is readily oxidized at the anode to produce electricity. The reformer provides enough hydrogen supply for efficient fuel cell operation at 600 mV with 0.2 A cm⁻² and a hydrogen stoichiometric ratio of 1.2 ($\lambda_{H_2} = H_2 \text{ fed}/H_2 \text{ reacted} = 1.2$). However, unreacted MeOH (~5 %) in combination with low H₂ content poisons the anode electrode and the cell performance rapidly decreases. Gradual recovery of the initial performance under pure H₂ is observed after switching to pure H₂. A slight improvement of the cell's design by the introduction

of a pre-reforming step significantly improves the electro-catalytic behavior.

Keywords High-temperature PEM fuel cell · Internal reforming · Methanol · Hydrogen · Copper catalyst

1 Introduction

Reforming methanol fuel cell (RMFC) is a type of indirect methanol fuel cell, which first converts methanol into hydrogen with a methanol reformer [1–5], and then the hydrogen rich gas is sent to a hydrogen/air fuel cell to generate electricity. The process of methanol reforming must be carried out at 250–300 °C in order to obtain about 90 % fuel conversion efficiency and 50 % hydrogen concentration. However, the state-of-the-art hydrogen/air fuel cell in the RMFC can operate only between 160 and 180 °C. There is a mismatch of the operating temperature ranges between the fuel cell and the reformer. In addition, there are two subsystems in a common RMFC, i.e., the reformer and the fuel cell. Therefore, many auxiliary components are needed for each of the subsystems. Furthermore, these components not only consume additional energy but also increase the total system weight. Only 40–50 % energy efficiency can be obtained by reforming methanol to hydrogen, and about 50–60 % of this energy can be converted from the hydrogen rich gas to electricity in the fuel cell. Therefore, the final energy efficiency is less than 30 % in a traditional RMFC [3]. In order to alleviate the problems in the traditional RMFC, we have recently proposed [1, 4, 5] the development of an internal reforming methanol high-temperature PEM fuel cell (IRMFC) with a bi-functional anode electrode, which consists of two layers (Fig. 1). The first layer's function is to reform

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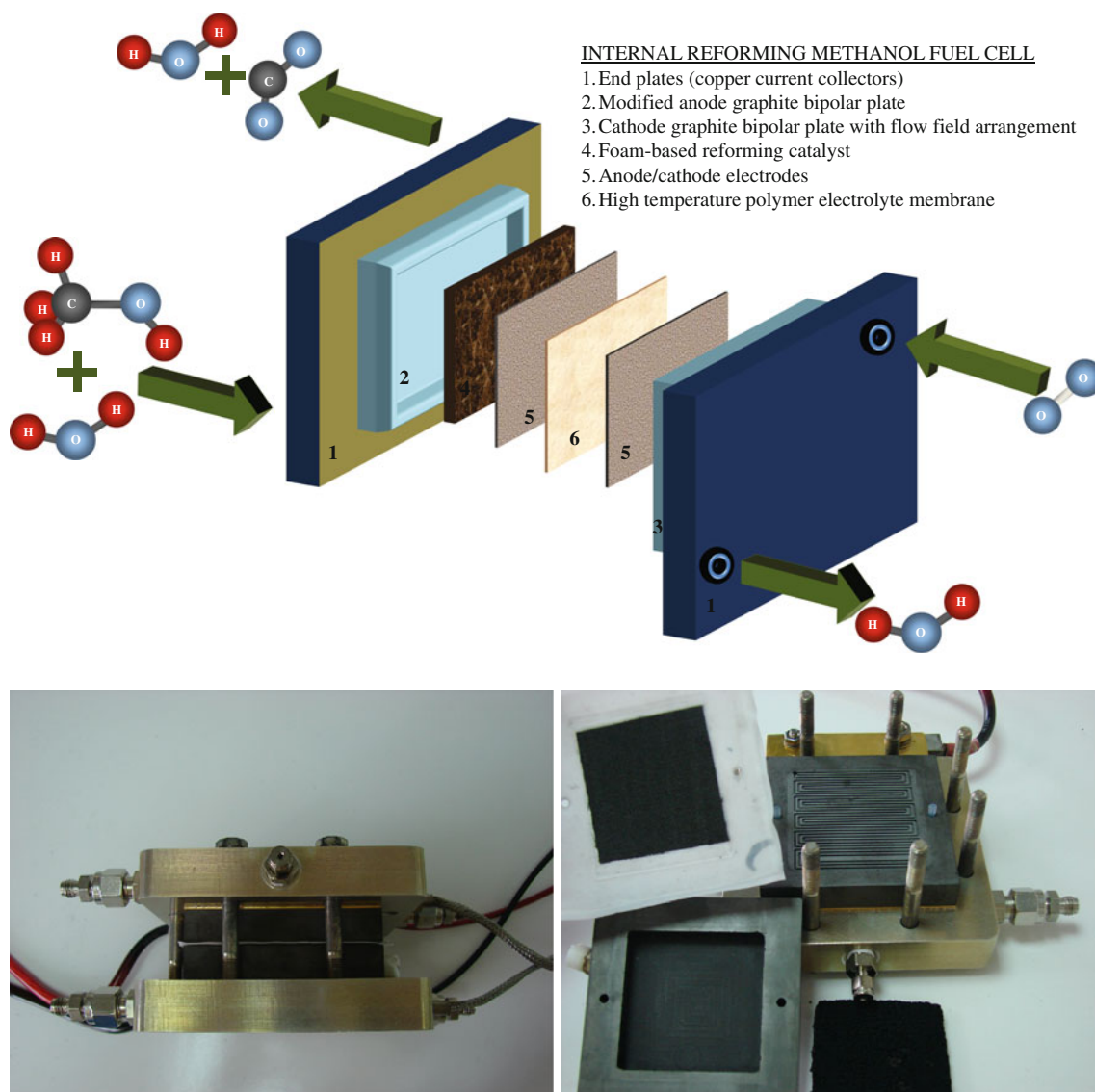


Fig. 1 IRMFC configuration

methanol, and the second layer's function is to catalyze hydrogen oxidation. The advantages of the IRMFC with a bi-functional anode are: compact system configuration, simple balance of plant, higher power and energy efficiencies, and lighter weight. There is no heat loss between the methanol reforming layer and the hydrogen oxidation layer since the heat produced by the oxidation of the produced H_2 is readily used by the reforming catalytic layer within the anode compartment. Among various fuels the direct and efficient processing of methanol has been considered as a potential alternative due to (i) high volume energy density, (ii) low sulfur content, (iii) safe handling/storage, (iv) relatively low reforming temperatures, (v) low CO formation, and (vi) possible production from renewable sources.

However, the key technology for the IRMFC with bi-functional anode relies on high-Temperature electrolyte membranes that are highly conductive at 180–200 °C and are developed by Advent Technologies S.A. [5–7]. These advances in the design and development of polymer electrolyte membranes and electrocatalysts (e.g., new high-Temperature polymer electrolytes impregnated with H_3PO_4 : ADVENT TPS[®] MEA) allow the operation of PEMFCs at temperatures in the range 180–200 °C, whereas (i) CO tolerance and functionality of the anode is highly improved, (ii) reaction rates are enhanced, and (iii) heat and water management are simplified.

In the present study, an internal reforming methanol single fuel cell was prepared and the electrochemical characterization of materials (MEA and reforming catalyst)

and cell performance was evaluated at atmospheric pressure under various feedstreams in the absence and in the presence of reformer. Special attention has been paid on the effect of unreacted methanol on the MEA's performance.

2 Experimental procedure

2.1 Membrane electrode assembly

In the present work, an ADVENT TPS[®] MEA was employed. A detailed description of the MEA preparation procedure has been reported previously [4, 6, 7]. The MEA has the following characteristics: (i) PPy(60)coT(40)S copolymer film of 180–200- μm thickness with 180–200 wt% H_3PO_4 doping level, (ii) 22- cm^2 electrode active area with a platinum loading of 1.5 mg Pt/ cm^2 (for each electrode) and a ratio of 2 g H_3PO_4 /g Pt. MEAs were fabricated by hot pressing the Pt/C electrodes to the acid-doped polymer electrolyte membrane at 150 °C for 15 min in a die setup using PTFE and FEP gaskets to achieve the appropriate compression and sealing in the single cell.

2.2 Reforming catalyst

CuMnOx ($\text{Cu}/(\text{Cu} + \text{Mn}) = 0.30$) and CuMnAlOx methanol-reforming catalysts supported on Cu metal foam [1] were prepared via the in situ combustion method offering a wide variety of advantages over packed beds for fuel processor catalytic operation mainly related to reduced pressure drop, mechanical integrity, improved heat transfer and reduction in size. The Cu metal foam used in this study is a commercial product of Changsha LYRUN New Material Co., Ltd., with a porosity of 30 ppi (pores per linear inch), 10 mm thickness and 4,000 g/ m^2 density. For experimental purposes, each foam was cut into pieces of appropriate dimensions (i.e., $5 \times 5 \times 0.3\text{--}1\text{ cm}^3$). The Cu metal foam was immersed for a few seconds in an aqueous solution of urea and nitrate salts of copper and manganese, mixed in the appropriate molar ratios [1, 8–10]. Thereafter, the foam was removed and the excess solution was blown out by hot air ejected from a heat gun set at 150 °C. The temperature of the heat gun was subsequently raised to 500 °C and immediately the combustion reaction started. This procedure was repeated several times to achieve the desired catalyst loading. The surface of the foam catalyst was further coated with a thin layer of carbon/Teflon (70/30) paste to minimize contact resistance since the reformer also plays the role of current collector in direct contact to the anode electrocatalyst. The reforming catalyst was pre-reduced at 350 °C under H_2 flow.

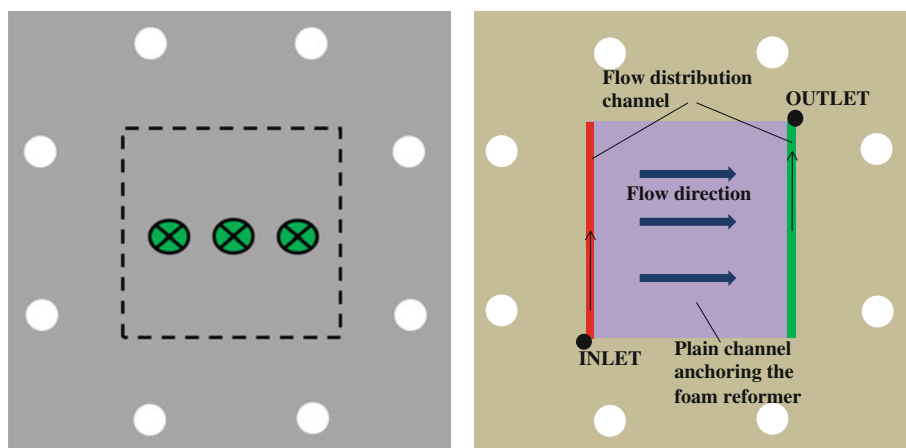
2.3 Fuel cell measurements

An internal reforming methanol single fuel cell (Fig. 1) was prepared according to the configuration described in detail in previous reports [1, 4, 5]. The employed single cell has the following features: (i) stainless steel end plates, (ii) copper foam-supported reforming catalyst which also plays the role of current collector, (iii) triple serpentine flow field arrangement for the cathode on a Poco[®] graphite end plate, and (iv) ADVENT TPS[®] MEA described in Sect. 2.1. A standard single cell was purchased from Fuel Cell Technologies Inc., to be modified in such a way to fit the foam-reforming catalyst (Fig. 1). The membrane electrode assembly comprising an ADVENT TPS[®] phosphoric acid doped copolymer, as the high-Temperature polymer electrolyte membrane, was sandwiched between the anodic (CuMnOx supported on metallic copper foam and placed adjacent to the Pt/C anode electrocatalyst) and the cathodic end plate. Vaporized methanol and water mixtures were supplied to the anode compartment where the reforming catalyst is directly adjoined with the anode electrode. The cell temperature was set at 200 °C. The electrochemical characterization of materials (MEA and reforming catalyst) and cell performance was evaluated at atmospheric pressure under various feedstreams in the absence and in the presence of the copper foam-supported reforming catalyst. Product analysis was carried out using a gas chromatograph (Agilent Technologies, 6820 GC System) equipped with TCD and FID. The electrochemical measurements (polarization and ac impedance) were carried out using an AUTOLAB PGSTAT30 potentiostat/galvanostat. Impedance data were obtained within a frequency range from 50 kHz to 0.02 Hz. The stimulus amplitude was 5 % of the applied current in galvanostatic impedance experiments and 0.05 mV in potentiostatic impedance experiments.

2.3.1 Catalytic measurements and gas distribution along the reformer

Methanol's conversion and concentration distribution along the side of reformer attached to the anodic electrode was investigated in a special single cell fixture (Fig. 2) without the presence of the MEA. The MEA was removed and the cathodic graphitic plate was substituted by a plate that covers the foam-supported catalytic bed bearing three septum valves that were placed along the flow direction of the reformer at 1.25, 2.5, and 3.75 cm away from the inlet. Aliquots of the reaction mixture were sampled from the three septum valves by means of a gas syringe to the gas chromatograph. A highly active CuMnAlOx catalyst [11] supported on Cu foam (4.5 g catalyst loading; reformer dimensions: $5 \times 5 \times 0.3\text{ cm}^3$) was placed in a typical

Fig. 2 Top view of modified cathode plate (*left*) without flowfield and three septum valves (*times within circle*) at 1.25, 2.5, and 3.75 cm for gas sampling from the upper side of reformer (*dashed line*). Anode plate (*right*) flowfield configuration (*top view*) typical pocket plate without flowfield at the bottom side of reformer ($5 \times 5 \times 0.3 \text{ cm}^3$)



pocket plate so that the reacting gases flow along one direction within the Cu foam catalytic bed similar to the flow distribution in the anodic compartment of the IMRFC. The activity data were obtained at two different reaction temperatures, i.e., 200 and 210 °C.

3 Results and discussion

3.1 Electrochemical testing of electro/reforming anodes

The internal reforming methanol fuel cell's steady state performance was examined by means of I–V steady state polarization measurements. Electrochemical impedance spectroscopy was also employed as a powerful diagnostic tool for the separation and quantification of three sources of

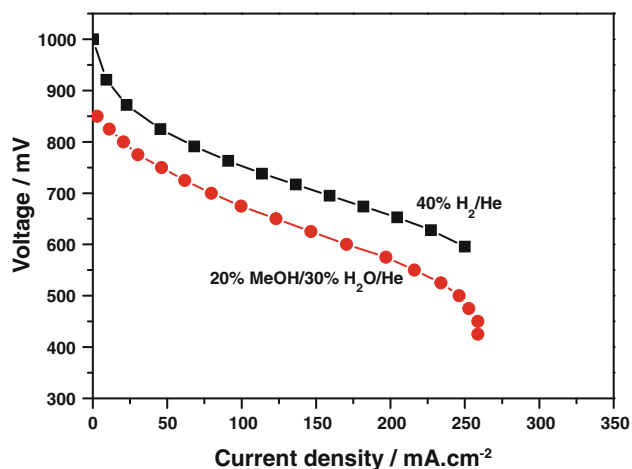


Fig. 3 Polarization curves obtained at 200 °C in an IRMFC composed of ADVENT TPS® MEA (22-cm² active area) and 4.5 g of CuMnOx on Cu foam (3-mm thickness) for two different feedstreams. 40 % H₂/He (*filled square*); 20 % MeOH/30 % H₂O/He (75 % MeOH conversion at 600 mV), W/F = 2.455 g s cm⁻³ (*filled circle*)

polarization: charge transfer activation or “kinetic” losses, ion and electron transport or “ohmic” losses, and concentration or “mass transfer” losses. Typical polarization curves (Fig. 3) and (galvanostatic) impedance spectra (Fig. 4) measured at 200 °C under MeOH/H₂O anode feedstreams (cathode feed: pure oxygen) were obtained in an internal reforming methanol single cell composed of ADVENT TPS® MEA and CuMnOx/Cu foam. Hydrogen produced by the steam reforming of methanol readily interacts with the Pt/C electrode resulting in the I–V curve depicted in Fig. 3. It is worth noticing that similar performance was obtained in our previous study [1], but with a thicker foam (10 vs. 3 mm in the present study) and at four times higher contact time. The lower performance with respect to pure hydrogen can be initially attributed to the lower H₂ partial pressure (35 %) that is being produced by the reforming reaction. The utilization of the produced H₂ is 76 % at 0.2 A cm⁻² and limiting current is reached at 0.26 A cm⁻² due to H₂ starvation. It must be noted that in the present case of the thinner foam, a significant improvement in the enhancement of methanol-reforming reaction rate was observed as compared with the thicker foam configuration reported previously [4]. Specifically, at OCV, methanol conversion reached 45 %; while at 600 mV and 0.17 A cm⁻², methanol conversion was enhanced to 75 %. This corresponds to 66 % increase in the conversion of methanol and H₂ production rate and can be attributed to the more efficient removal of H₂ from the catalytic bed through the fuel cell reaction, thus resulting in the effective enhancement of the reforming reaction rate by a larger portion of the reforming catalyst. It should be noted that the beneficial effect of the combined fuel cell and reformer operation in the anode compartment enables the decrease of contact time, i.e., the decrease of reforming catalyst loading.

Figure 4 shows AC impedance spectra recorded under load depicting the polarization characteristics of the MEA under methanol/water feed and the transition to H₂ flow. The typical equivalent circuit used for the single cell is

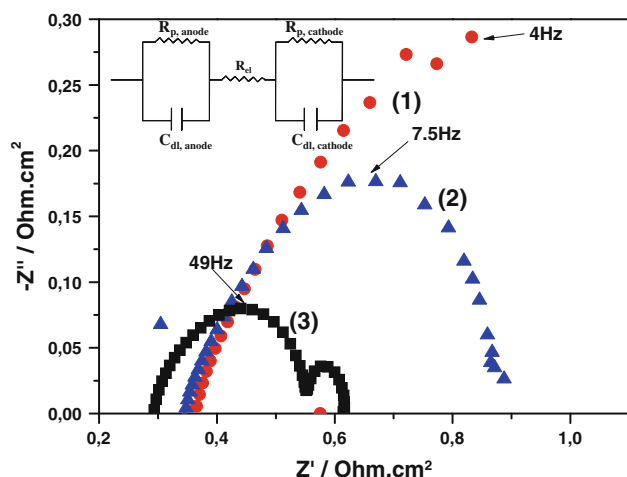


Fig. 4 Effect of MeOH/H₂O mixture on the electrochemical behavior of internal reforming methanol single cell composed of ADVENT TPS® MEA (22 cm² active area) and 4.5 g of CuMnOx on Cu foam (3 mm thickness). Impedance spectra were obtained at 200 °C and 0.12 A cm⁻² under 1 20 %MeOH/30 %H₂O/He (W/F = 2.455 g s cm⁻³; 600 mV at 2.7 A) and after switching to pure H₂ (2 738 mV at 2.7 A, and 3 728 mV at 2.7 A after 15 h). Cathode feed: pure oxygen ($\lambda_{O_2} = O_2$ fed/ O_2 reacted = 2). Inset equivalent circuit. R_{el} = ionic resistance of the membrane, R_p = polarization resistance, C_{dl} = double-layer capacitance

shown as inset of Fig. 4. The polarization curve (Fig. 3) and the features of the Nyquist plots of the impedance data (Fig. 4) change dramatically in the presence of methanol/water feed. The high-frequency resistance (left intercept of the Nyquist plots with the real axis in Fig. 4), which represents the total ohmic resistance of the fuel cell, is higher in the presence of methanol in the anode stream strongly indicating a significant negative effect of methanol on the ionic conductivity of the membrane. Indeed, the ionic resistance of the membrane is 0.295 Ohm cm² in the presence of pure hydrogen, while the presence of methanol/water stream results in a higher R_{el} equal to 0.365 Ohm cm². In addition, the polarization resistance is being significantly affected and as it will be shown further on this can be attributed to the poisoning effect of adsorbed methanol species on the anode catalyst. Postmortem XRD and EDX analysis of several samples did not show any indication of reaction of methanol with phosphoric acid to form methyl phosphate. It should be also noted that methanol crossover was observed during fuel cell operation (CO₂ production was detected at the cathode outlet, while traces of methanol were detected when the cathode stream was switched to pure helium) and further investigation is under way. By switching the anode feed to pure hydrogen, a slow return to the initial state under H₂ flow is being observed (Fig. 4). Spectrum “3” was recorded after 15 h upon switching to pure H₂ flow, indeed showing a slow recovery of the performance of the cell. This strongly

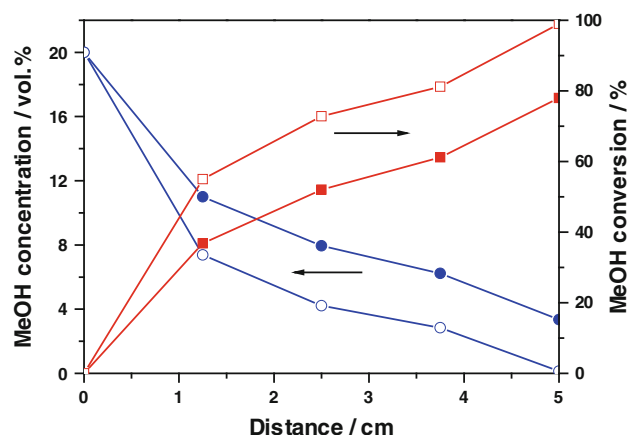


Fig. 5 Methanol conversion (filled square) and mole fraction (filled circle) distribution along the flow direction of the Cu foam catalytic reformer. Reformers: 4.5 g of CuMnAlOx on Cu foam. A pocket-like plate is employed for supporting methanol reformer. (W/F) = 2.455 g s cm⁻³; $T = 200$ (solid symbols) and 210 °C (open symbols); 20 % MeOH/30 % H₂O/He

indicates a reversible process that involves slow removal of species (methanol or intermediates), which are either interacting with the electrolyte membrane or the anode catalyst.

Methanol conversion and concentration profile along the catalytic foam reaction pathway was measured in a separate fixture, which was designed to select aliquots along the flow direction (see Sect. 2.4). As shown in Fig. 5, though the reforming reaction attains high conversion at the reactor exit, the inlet part of the catalytic reformer suffers from high methanol concentrations which will be further discussed as affecting in a negative way the performance of the MEA.

In order to overcome the negative effect of unreacted methanol at the inlet, a Kapton film (2.5 × 5 cm² × 30 μm thickness) was placed on the upper inlet side of the foam reformer covering half of the contact area between the foam reformer and the MEA anode, thus allowing for a pre-reforming reaction compartment so that the high amounts of unreacted methanol are not allowed to poison the performance of the MEA. In this respect, in the current density calculations, we consider only 11 cm² of MEA's active area out of the 22 cm² without the Kapton film. The obtained AC spectra and I–V curves are shown in Fig. 6. Pre-reforming of methanol significantly improved the cell performance (0.2 A cm⁻² at 600 mV) as compared to the corresponding results in the absence of Kapton film. The lower methanol conversion obtained in the presence of Kapton film is attributed to the lower enhancement of methanol reforming reaction due to the almost half H₂ pumping by the MEA, as only half of MEA's active area is operating.

The parts of the Cu foam reformer close to the entrance of the reacting gases with the high methanol concentration do not any longer affect the ionic resistance of the MEA.

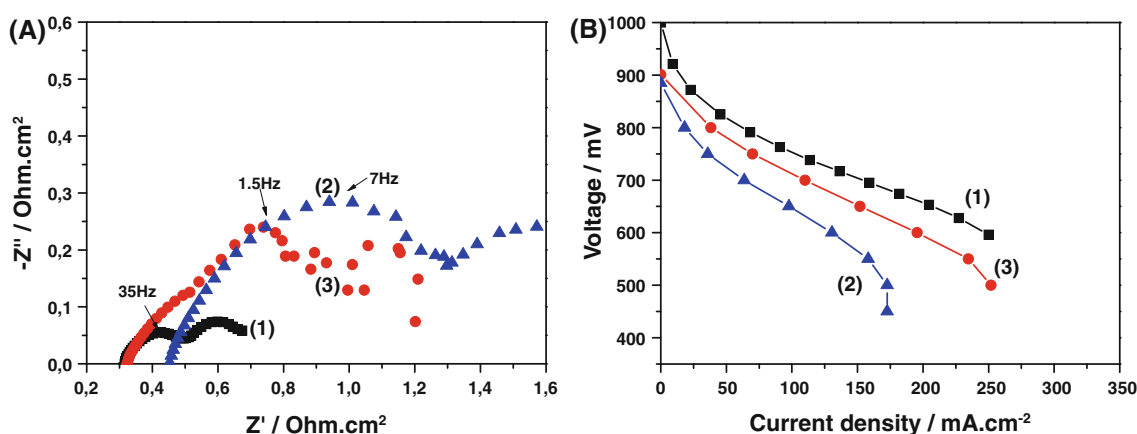


Fig. 6 Effect of pre-reforming reaction (allowed via the placement of a Kapton film at the interface of reformer/MEA; Half of the active area of 22 cm² at the inlet side is covered by the Kapton film) on the electrochemical performance monitored via impedance spectra (a) at 600 mV and polarization curves (b) of an internal reforming

As it will be discussed in the next section, the lower concentration of the unreacted methanol that is facing the MEA is below the concentration threshold that affects the ionic conductivity of the membrane.

Taking into account the strong acidic environment and possible dissolution of copper catalyst into the electrolyte, separate stability tests (500 h) have been performed [11] in the presence and absence of MEA. Taking into account the thickness of the reformer (ranging from 10 to 3 mm), the morphology of the top surface of reformer was slightly different in color from the bottom and mid part of the reformer. Thus, a modification of the physicochemical nature of the copper is possible, nevertheless it was not observed by XRD or EDX. However, such a modification is limited in a small area of the top surface of the foam-based reformer and cannot determine the overall behavior, especially in experiments lasting less than 10 h.

3.2 Effect of methanol on the electrochemical performance of the MEA

The effect of methanol on the electrochemical performance of MEA was studied in separate experiments in the absence of reformer (Fig. 7). It has to be noted that the employed MEAs have been tested for their stability at 200 °C under H₂/air feed and after 170 h stable operation, there was a degradation rate <0.15 mV h⁻¹. Typical (galvanostatic) impedance spectra measured at 200 °C, 0.2 A cm⁻², λ_{H_2} = H₂ fed/H₂ reacted = 1.2 under different anode feedstreams (cathode feed: pure oxygen, λ_{O_2} = 2) in the absence of Cu foam reformer are presented in Fig. 7. As it is explicitly shown in Fig. 7, the effect of methanol on cell performance depends on the H₂/methanol mole fraction ratio, thus showing the competitive interaction of H₂ and methanol.

methanol single cell composed of ADVENT TPS[®] MEA and sintered 4.5 g of CuMnAlOx on Cu foam. (W/F) = 4.909 g s cm⁻³; T = 200 °C; 20 % MeOH/30 % H₂O/He; (1) 40 % H₂/He (filled square); (2) without Kapton film, 83 % MeOH conversion (filled triangle); (3) with Kapton film, 63 % MeOH conversion (filled circle)

The presence of 5 % MeOH in a hydrogen-lean gas mixture significantly modifies the electrochemical features of the MEA in a negative way. The total ohmic resistance of the fuel cell, determined by the high-frequency intercept of the Nyquist plots in Fig. 7, increases abruptly and significantly shifts to higher values by feeding with 40 % H₂ and 5 % methanol in the anode stream showing a significant effect of methanol on the ionic conductivity of the membrane. In addition, the polarization resistance is being significantly affected too, implying a poisoning effect of adsorbed methanol species on the catalyst. The corresponding resistance values obtained from the Nyquist plots in Fig. 7 are given in Table 1.

A trivial effect is observed at higher H₂ partial pressure or correspondingly at lower methanol concentration (Fig. 7c, d). It is reasonably expected that the ionic conductivity of the membrane must be affected due to the methanol crossover through the membrane. However, at higher H₂ partial pressure, almost no effect on the conductivity is observed for 5 % MeOH concentration (Fig. 7c; Table 1). This is a quite interesting observation and the reason for this can be sought in two distinct processes: (i) The conductivity is affected due to the interaction of a polar molecule like methanol with the H₃PO₄/polymer matrix thus resulting in stronger hydrogen bonds and (ii) the blocking of charge transfer pathways of the protons at the electrochemical interface due to the strong adsorption of methanol on the catalyst, inducing the increase in the polarization resistance too. In the first case, a competitive process that incorporates direct H₂ interaction on the conductivity of the membrane must be considered to explain the positive effect of the higher partial pressure of H₂ at the same methanol feed composition (5 %, Fig. 7c; Table 1). Such direct interaction has been proposed in the past for the interpretation of bistability phenomena observed with

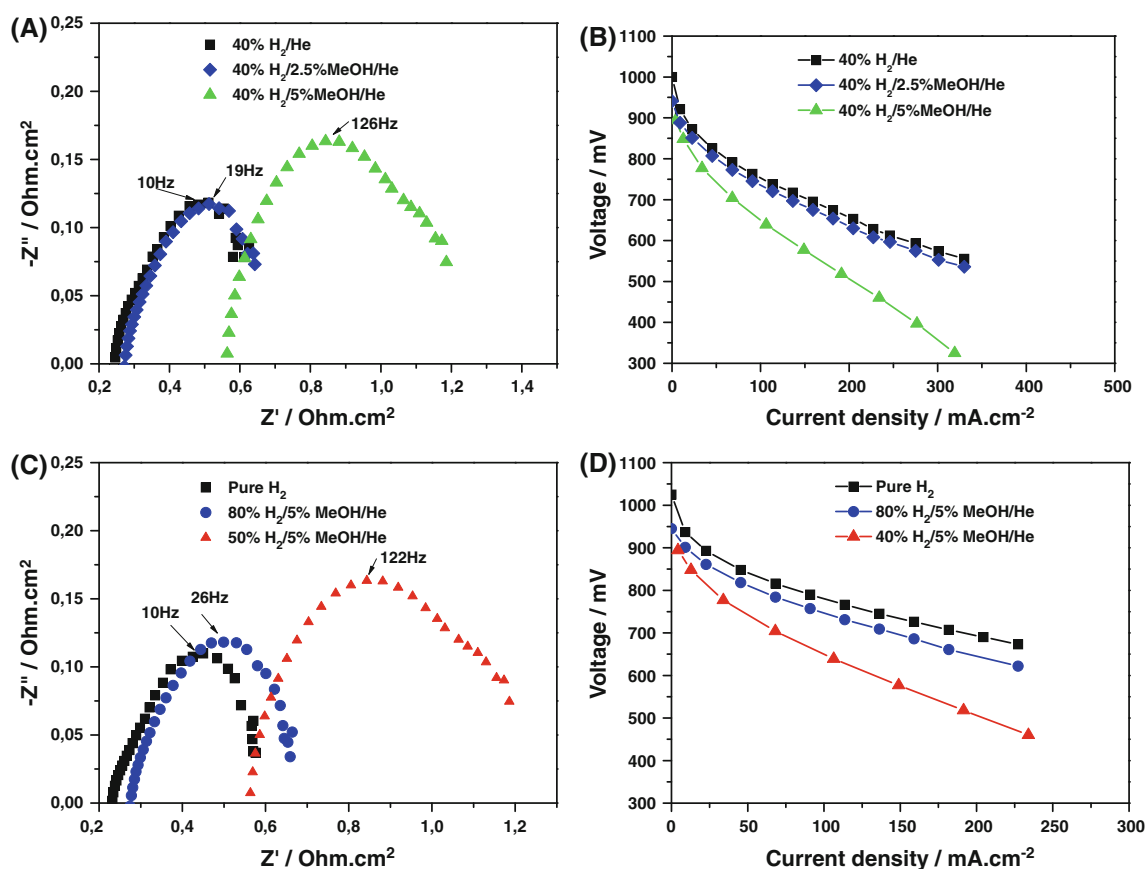


Fig. 7 Effect of MeOH/H₂O concentrations on the electrochemical performance of ADVENT TPS[®] MEA (22 cm² active area). Impedance spectra (a, c) and polarization curves (b, d) obtained in a single cell at 200 °C. AC data at 0.2 A cm⁻², $\lambda_{\text{H}_2} = 1.2$, $\lambda_{\text{O}_2} = 2$ (pure O₂). The following anode feedstreams were employed: a, b 40 % H₂/He

(filled square), 40 % H₂/2.5 % MeOH/He (filled diamond), 40 % H₂/5 % MeOH/He (filled triangle). c, d Pure H₂ (filled square), 80 % H₂/5 % MeOH/He (filled circle), 40 % H₂/5 % MeOH/He (filled triangle)

Table 1 Ionic resistance of the electrolyte and polarization resistance of a single cell loaded with ADVENT TPS[®] MEA (22 cm² active area) and operated at 200 °C under various anode feedstreams (He as balance).

H ₂ concentration, %	MeOH concentration, %	R_{el} Ohm cm ²	R_{p} Ohm cm ²
40	0	0.244	0.379
40	2.5	0.275	0.387
40	5	0.562	0.668
100	0	0.232	0.348
80	5	0.278	0.389
50	5	0.560	0.65

Data obtained from impedance spectra in Fig. 7 at 0.2 A cm⁻², $\lambda_{\text{H}_2} = 1.2$, $\lambda_{\text{O}_2} = 2$ (pure O₂)

NAFION MEAs by Katsaounis et al. [13]. They proposed a proton tunneling conduction mechanism, which is affected both by the partial pressure of the gas phase H₂ and by the applied potential. Certainly, in the present case, further investigation is needed to reach more solid conclusions

especially for the competitive interaction of methanol and H₂ on proton conductivity.

4 Conclusions

The most important aspect of integration of IRMFC components into a functional unit refers to incorporation and efficient operation of the reforming catalyst in the anode compartment of the cell. The polarization curves and the characteristics of the impedance spectra of the proposed IRMFC significantly changed in the presence of methanol in the hydrogen stream, implying a poisoning effect of adsorbed methanol species on the electrocatalyst and the proton conductivity of the membrane. Pre-reforming of methanol significantly improved the cell's performance (0.2 A cm⁻² at 600 mV). The negative effect of methanol is still an issue to be solved and higher methanol conversion should be achieved (Al-doped CuMnOx catalyst offers that possibility since it is two times more active than the undoped catalyst [11]). In addition, operation at 210 °C

with new membranes developed by Advent is expected to improve MeOH tolerance [12]. Alternative anode flowfield configurations (e.g., feed stream inlet from the bottom center of the foam or inlet flowfield at the bottom side of the foam with gradual decrease (increase) of the channels (foam) depth (thickness)) are currently under construction and will be investigated.

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